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AUTHOR: Zamkov, V. A.

TITLE: Thermodynamics of the critical effects in an electric field

PERIODICAL: Moscow. Universitet. Vestnik. Seriya III. Fizika,
astronomiya, no. 6, 1962, 32-36

TEXT: The formula $\epsilon - n^2 = \frac{2\pi N \bar{m} \bar{m}^*}{V_c k T_c (\epsilon - 1)} \cdot \frac{B}{B+1}$ is derived for sufficiently small $T - T_c$ and large ϵ on the basis of the general Fröhlich relation

$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = \frac{4\pi N \bar{m} \bar{m}^*}{3V_c k T_c}$. Here ϵ is the dielectric constant, n is the refractive index, N is the number of cells in the volume V of molecules or molecule groups with equal mean polarizability in an external field, \bar{m} is the moment of the cell in the substance which is determined by the configuration of more closely interacting molecules, \bar{m}^* is the moment of an arbitrary sphere polarized by a cell \bar{m} in it. The subscripts c indicate the critical values, $\tau = T/T_c$ is the reduced temperature, B is a constant depending on

Card 1/4

Thermodynamics of the critical...

S/188/62/000/006/007/016
B187/B102

the equation of state ($B = 2/3$ for van der Waals). It can be seen that ϵ passes a maximum for $V = V_c$ and $T = T_c$. Scaife (Proc. Phys. Soc., 69B, 153, 1956) has given a formula for the pressure p in a uniform electric field E . This formula is used to derive an expression for the modulus of compression $1/\chi$, which contains a factor of $(\tau - 1)$ squared and which therefore has to vanish when the critical values for two values of τ_1 and τ_2 have been reached.

$$\tau_{1,2} - 1 = AE^2 \pm E \sqrt{(AE)^2 + B^2}, \quad A = \frac{(n^2 - 1)(n^2 + 2)}{72\pi p_c}, \quad B = \frac{N \bar{m} \bar{m}^*}{6p_c V_c k T_c}$$

For nonpolar substances a slight variation ensues in proportion to E^2 . For highly polar substances ($B^2 \gg A$) the displacement of the critical temperature goes linearly with the field strength. For molecules with a strong dipole

an estimation gives $BE \sim \frac{\mu E}{\frac{3}{2} k T_c}$ and $AE^2 \sim \frac{\alpha E^2}{\frac{3}{2} k T_c \cdot 1082}$, where μ is the dipole

Card 2/4

Thermodynamics of the critical...

S/188/62/000/006/007/016
B187/B102

moment of the free molecule, α is the polarizability. The increase of T_c in an electric field is proportional to the ratio of the energy of the molecular dipole to the energy of the rotational degrees of freedom. The above estimates yield $RT_c/V_c P_c = 0.293$. This value agrees to three decimal places with the empirical results for noble gases as obtained by Guggenheim (Thermodynamics North Holl. publ. Co., 1957). An estimate gives $A \sim 0.0001 \text{ deg/v}$ and

$$B \sim \frac{A 10^{-2}}{2T_c} \sim 10^{-4} [\text{CGSE}]^{-1}.$$

It is supposed that condensation in the presence of an electric field along and across the field takes place at different temperatures. τ_1 is reached first which corresponds to a two-dimensional condensation in a plane perpendicular to the field. A meniscus does not appear when the electric field and the gravitational field have the same direction. When the fields are crossed condensation occurs immediately. This state is described exactly by the Onsager theory (Phys. Rev., 65, 117, 1944).

Card 3/4

Thermodynamics of the critical...

S/188/62/000/006/007/016
B187/B102

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SUBMITTED: March 20, 1962

Card 4/4